

# Relative Permittivity and Resistivity of Liquid HFC Refrigerants under High Pressure<sup>1</sup>

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## ABSTRACT

The static relative permittivity (dielectric constant) and the resistivity of HFC-236ea ( $\text{CF}_3\text{-CHF-CHF}_2$ ) and HFC-245fa ( $\text{CF}_3\text{-CH}_2\text{-CHF}_2$ ) in the liquid phase were studied at temperatures from 293 to 343 K and pressures from 0.1 to 50 MPa. The relative permittivity was measured by a concentric cylinder type capacitance cell with an LCR-meter with an uncertainty less than 0.1%. The resistivity was measured by a high resistance meter using plane-parallel platinum electrodes installed in a borosilicate glass syringe. It was found that the relative permittivities and the resistivities of liquid HFC-236ea and HFC-245fa at 303 K and 0.101325 MPa are about 5.13 and 6.54, and  $1.5 \times 10^{10}$  and  $0.2 \times 10^{10} \Omega \cdot \text{cm}$ , respectively. The relative permittivity and the resistivity increases with increasing pressure and decreasing temperature monotonously.

**KEY WORDS** : dielectric constant, electrical resistivity, hydrofluorocarbon, permittivity, pressure, refrigerant

## 1. INTRODUCTION

The relative permittivity and the resistivity of environmentally acceptable refrigerants are necessary to study and interpret the electrical properties of these polar fluids, and to give operational values for some of the design parameters of machinery used in air conditioning and refrigeration industry. High electrical resistivity of working fluids is favorable in closed systems. The temperature, pressure and density dependences of these properties will also permit the application of molecular theories of polar fluids.

In this work the relative permittivity and the resistivity of HFC-236ea (1,1,1,2,3,3-hexafluoropropane) and HFC-245fa (1,1,1,3,3,-pentafluoropropane) in the liquid phase have been measured at temperatures from 293 to 343 K and pressures from 0.1 to 50 MPa. HFC-236ea has been proposed as replacement for CFC-114. HFC-245fa is one of leading candidates for a new blowing agent for rigid polyurethane foams as replacement for HCFC-141b.

## 2. EXPERIMENTAL

The relative permittivity was measured by a three-terminal concentric cylinder type capacitance cell. The apparatus and procedure have been described in detail in a previous work [1]. Capacitance measurements were made with a multi-frequency LCR-meter (YHP 4274A) using 100 kHz with an uncertainty less than 0.1%.

The resistivity measurements were carried out with plane-parallel platinum electrodes (area=1 cm<sup>2</sup>, electrode separation=0.3 cm). The electrodes were equipped in a borosilicate glass syringe in order to avoid the contamination of the samples. The resistivity was measured by a high resistance meter (HP 4339A) under the voltage of 10V and at the frequency of 60Hz in order to suppress the electroconvection and the polarization at the electrodes. The instruments were thermostatted in a liquid bath controlled within  $\pm 0.03$  K. The temperature was measured using a platinum resistance thermometer with an accuracy of 0.01 K. Pressure was measured with a Heise Bourdon gauge and a strain gauge type pressure transducer with an accuracy of 0.1%. The capacitance cell was calibrated using the standard relative permittivity values of benzene and cyclohexane at temperatures from 298 to 323 K. The cell constant of the resistivity cell was determined using the reference aqueous solution of KCl.

The sample fluids of HFC-236ea and HFC-245fa were supplied by Daikin Industries, Ltd., and had a purity of 99.9 mol%. These samples were used without further purification. Benzene and cyclohexane were obtained from commercial sources with a specification of minimum purity of 99.9%. They were used after purification by the fractional crystallization.

## 3. RESULTS AND DISCUSSION

### 3.1. Static Relative Permittivity

The static relative permittivity of a liquid,  $\epsilon$ , is defined by the ratio of the capacitance between two electrodes filled with the liquid  $C$ , to that in vacuum,  $C_0$ ,

$$\epsilon = C/C_0 \quad (1)$$

The experimental data for HFC-236ea and HFC-245fa are shown in Figs.1 and 2, respectively, as functions of temperature and pressure. In both cases, every isotherm increases monotonously with increasing pressure with a slight negative curvature. In

these experimental conditions, the relative permittivity decreases almost linearly with increasing temperature along each isobar. The relative permittivity of HFC-245fa is systematically larger than that of HFC-236ea at the same condition. However, the pressure coefficient of the relative permittivity  $(\partial\varepsilon/\partial P)_T$  is quite similar each other.

The isotherm of  $\varepsilon$  against pressure can be represented by several empirical expressions. The Owen-Brinkley equation [2,3] is a representative one.

$$\frac{\varepsilon - \varepsilon_0}{\varepsilon} = C \ln \left( \frac{B + P}{B + P_0} \right) \quad (2)$$

where  $\varepsilon_0$  is the relative permittivity at a reference pressure  $P_0$ , and  $P$  is the pressure in MPa. The coefficient  $C$  and  $B$  were determined by the least square fitting. The empirical coefficients are given in Tables I and III together with the mean and the maximum deviations of the experimental data from Eq.(2).

In Fig.3, the pressure dependences of the relative permittivity at 298.15 K for several fluorocarbon refrigerants in the liquid phase are compared. Judging from the molecular structures of these refrigerants and the electronegativities of F(4.0), Cl(2.5) and H(2.1), it is quite reasonable that the relative permittivity of HCFC-141b ( $\text{CH}_3\text{-CCl}_2\text{F}$ ), whose molecular structure is quite asymmetric is decisively larger, and that of CFC-113 ( $\text{CClF}_2\text{-CCl}_2\text{F}$ ) is clearly smaller than those of HCFC-123 ( $\text{CHCl}_2\text{-CF}_3$ ), HFC-236ea ( $\text{CF}_3\text{-CHF-CHF}_2$ ), HFC-245fa ( $\text{CF}_3\text{-CH}_2\text{-CHF}_2$ ), HCFC-225ca ( $\text{CHCl}_2\text{-CF}_2\text{-CF}_3$ ) and HCFC-225cb ( $\text{CHClF-CF}_2\text{-CClF}_2$ ). Among four halogenated propane derivatives, HFC-236ea and HFC-245fa have larger relative permittivities than HCFC-225ca and -225cb since the formers have more hydrogen atoms and the molecular structures are more asymmetric than the latters.

From the theory of molecular polarisability developed by Kirkwood [4] after the definition of Onsager's local field in a liquid assembly of permanent dipoles [5], it is possible to correlate the relative permittivity of the polar liquid with the apparent dipole moment  $\mu^*$  through the equation [6,7] :

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \left( \frac{M}{\rho} \right) = \frac{N_0}{3} \left( \alpha + \frac{\mu^{*2}}{3\varepsilon_0 k_B T} \right) \quad (3)$$

where  $M$  is the relative molar mass,  $N_0$  is the Avogadro number,  $\alpha$  is the molecular polarisability,  $\varepsilon_0$  the relative permittivity of vacuum and  $k_B$  the Boltzmann constant. The density  $\rho$  of HFC-236ea was calculated from the equation of state by Defibaugh and Silva [8,9]. The value of  $\mu^*$  was calculated for HFC-236ea by a linear regression of the Kirkwood function as a function of  $1/T$ . It was found that HFC-236ea has an apparent dipole moment  $\mu^*=2.50$  D.

### 3.2. Resistivity

In well-filtered liquids, charge carriers are ions or ionic associations of higher order (multipoles), which result from the spontaneous dissociation of tiny amounts of ionizable substances or of the action of natural radiation. Electron or hole conduction will never occur in the common situations because the electron life time is lower or

much lower than  $10^{-4}$  s, even in ultra purified liquids [10-12].

The volume conductivity  $\sigma=1/\rho$  of a medium containing  $i$  dissociable species generating a volume charge density  $q_i$  of free carriers of mobility  $k_i$  is

$$\sigma_0 = \sum k_i q_i \quad (4)$$

The resistivity is a characteristic of a dielectric fluid only at the thermodynamic equilibrium of charge carrier dissociation and recombination in the bulk, if the measuring conditions do not modify significantly the density and mobility of free carriers by displacement of the thermodynamic equilibrium, interfacial phenomena at the solid walls or electroconvection. If the applied voltage is low enough, the electric field  $E$  does not significantly disturb the thermodynamic equilibrium and Ohm's law is obeyed

$$j_0 = \sigma_0 E \quad (5)$$

$j_0$  being the current density. Therefore  $\sigma_0$  can be derived from the measurement of the current  $I_0$  flowing through the cell containing the sample liquid. If the voltage is applied for long enough time, the initial conduction current  $I_0$  decreases with time and the current reaches the limiting value  $I_s$ . The following relation is found between the initial conduction current  $I_0$  and the conduction current  $I$  at a time  $t$ .

$$I_0 = I (bt+1) \quad (6)$$

Therefore the genuine value of the conduction current  $I_0$  can be determined by extrapolation of time  $t$  to zero . The resistivity  $\rho$  is calculated from the resistance  $R=1/I$  by the following equation.

$$R = \rho (d/A) \quad (7)$$

where  $A$  is an area of plane-parallel electrodes and  $d$  the electrode gap distance.

As a check on the performance of the instrument, we measured first the resistivity of benzene and cyclohexane at temperatures from 298 to 323 K and pressures from 0.1 to 50 MPa. The experimental results are listed in Tables III and IV, respectively. Although experimental data are very scarce in the literature, our results at 298.15 K at atmospheric pressure are found to be consistent reasonably with literature values [13-15]. The progressive improvement in the purification techniques of dielectric liquids renders the measurement of their resistivity more and more difficult with conventional equipment especially at room temperature, or below [10]. In the present work the scattering of data are more remarkable at 298 and 303 K as compared with 313 and 323 K.

The numerical data of the resistivity of HFC-236ea and HFC-245fa are listed in Tables V and VI, respectively. The pressure and temperature dependences of the resistivity of HFC-236ea are shown in Fig.4. The behavior of the resistivity of HFC-245fa is similar to Fig.4.

The resistivity isotherm increases with increasing pressure monotonously with a small negative curvature. It may be due to the suppression of the charge carrier propagation

caused by the decrease of the intermolecular space with increasing pressure. The resistivity decreases with increasing temperature. It may be ascribed to the activation of Brownian movement of free ions between electrodes.

## CONCLUSIONS

New data for the relative permittivity and the resistivity of liquid HFC-236ea and HFC-245fa have been presented in the temperature range from 293 to 343 K, with pressures up to 50 MPa. Recently the authors have measured the density of liquid HFC-245fa. The details of the experimental results for the density and the data analysis of the relative permittivity of HFC-236ea and HFC-246fa in terms of the density dependence will be appeared elsewhere.

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Table I Empirical Coefficients in Owen-Brinkley Equation (2)  
for Liquid HFC-236ea

Temp. [K]	293.15	303.15	313.15	323.15	333.15	343.15
$P_0$ (MPa)	0.171	0.244	0.338	0.456	0.603	0.783
$\epsilon_0$ (-)	5.4038	5.1043	4.8161	4.5986	4.3946	4.1095
C (-)	0.15627	0.15271	0.14760	0.15571	0.15064	0.13721
B (MPa)	35.41	30.84	25.96	26.20	21.82	15.23
Max.dev.(%)	0.066	0.098	0.085	0.077	0.077	0.089
Mean dev.(%)	0.026	0.026	0.025	0.028	0.025	0.030

Table II Empirical Coefficients in Owen-Brinkley Equation (2)  
for Liquid HFC-245fa

Temp. [K]	298.15	303.15	313.15	323.15	333.15	343.15
$P_0$ (MPa)	0.152	0.182	0.254	0.347	0.466	0.613
$\varepsilon_0$ (-)	6.7134	6.5396	6.2036	5.8714	5.5538	5.2868
C (-)	0.15079	0.16240	0.13911	0.15452	0.15654	0.16428
B (MPa)	42.79	44.05	31.25	34.12	29.84	28.64
Max. dev.(%)	0.093	0.119	0.085	0.171	0.135	0.197
Mean dev.(%)	0.036	0.040	0.041	0.056	0.065	0.082

Table III Resistivity of Liquid Benzene

P* $\rho \times 10^{-13}$		P $\rho \times 10^{-13}$		P $\rho \times 10^{-13}$		P $\rho \times 10^{-13}$	
298.15 K		303.15 K		313.15 K		323.15 K	
0.10	0.902	0.14	0.846	0.10	0.800	0.10	0.737
10.1	1.06	10.0	0.966	10.0	0.919	10.0	0.890
20.0	1.22	20.1	1.10	20.0	1.03	20.1	0.992
30.1	1.30	30.1	1.16	30.0	1.10	30.0	1.05
40.0	1.43	40.0	1.31	40.0	1.18	40.0	1.13
50.1	1.52	50.0	1.35	50.0	1.22	50.0	1.20

\* P=pressure in MPa,  $\rho$ =resistivity in  $\Omega \cdot \text{cm}$

Table IV Resistivity of Liquid Cyclohexane

P*	$\rho \times 10^{-17}$	P	$\rho \times 10^{-17}$	P	$\rho \times 10^{-17}$	P	$\rho \times 10^{-17}$
298.15 K		303.15 K		313.15 K		323.15 K	
0.10	1.19	0.10	1.01	0.10	0.936	0.10	0.833
10.0	1.24	10.0	1.06	10.0	0.984	10.0	0.891
20.0	1.28	20.0	1.11	20.0	1.03	20.0	0.941
30.0	1.34	30.0	1.16	30.1	1.05	30.0	0.980
40.0	1.37	40.0	1.21	40.0	1.09	40.0	1.00
50.0	1.41	50.1	1.24	50.1	1.10	50.0	1.03

P\*=pressure in MPa,  $\rho$ =resistivity in  $\Omega \cdot \text{cm}$

Table V Resistivity of Liquid HFC-236ea

$P^* \times 10^{-10}$		$P \rho \times 10^{-10}$		$P \rho \times 10^{-10}$		$P \rho \times 10^{-10}$	
298.15 K		303.15 K		313.15 K		323.15 K	
5.02	1.49	5.04	1.46	5.03	1.37	5.00	1.28
10.2	1.53	10.1	1.47	10.0	1.38	10.0	1.29
20.0	1.56	20.0	1.50	20.1	1.39	20.0	1.31
30.1	1.60	30.1	1.53	30.0	1.42	30.4	1.32
40.1	1.63	40.0	1.56	40.1	1.43	40.0	1.34
50.0	1.66	50.0	1.57	50.0	1.45	50.3	1.35

$P^*$ =pressure in MPa,  $\rho$ =resistivity in  $\Omega \cdot \text{cm}$

Table VI Resistivity of Liquid HFC-245fa

$P^* \quad \rho \times 10^9$		$P \quad \rho \times 10^9$		$P \quad \rho \times 10^9$		$P \quad \rho \times 10^9$	
298.15 K		303.15 K		313.15 K		323.15 K	
0.13	2.00	4.99	1.95	5.05	1.63	5.01	1.44
5.00	2.05	10.0	1.99	10.0	1.67	10.0	1.48
10.1	2.09	20.0	2.09	20.0	1.76	20.0	1.55
20.1	2.19	30.1	2.15	30.0	1.83	30.0	1.61
30.1	2.24	40.0	2.21	40.1	1.89	40.0	1.67
40.0	2.31	50.0	2.27	50.2	1.95	50.0	1.71
50.0	2.36						

$P^*$ =pressure in MPa,  $\rho$ =resistivity in  $\Omega \cdot \text{cm}$

## FIGURE CAPTIONS

Fig.1 Static relative permittivity of liquid HFC-236ea as functions of temperature and pressure.

Fig.2 Static relative permittivity of liquid HFC-245fa as functions of temperature and pressure.

Fig.3 Static relative permittivity of liquid fluorocarbon refrigerants as function of pressure at 298.15 K.

Fig.4 Resistivity of liquid HFC-236ea as functions of temperature and pressure.

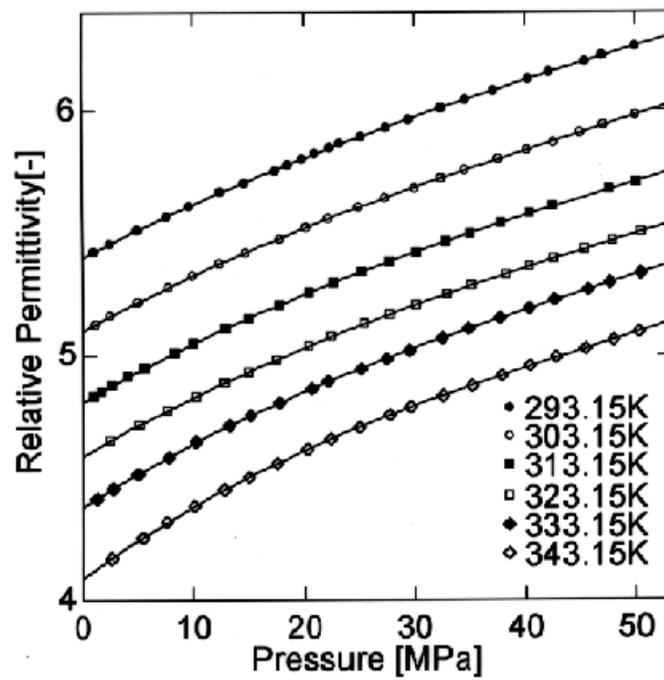


Fig.1

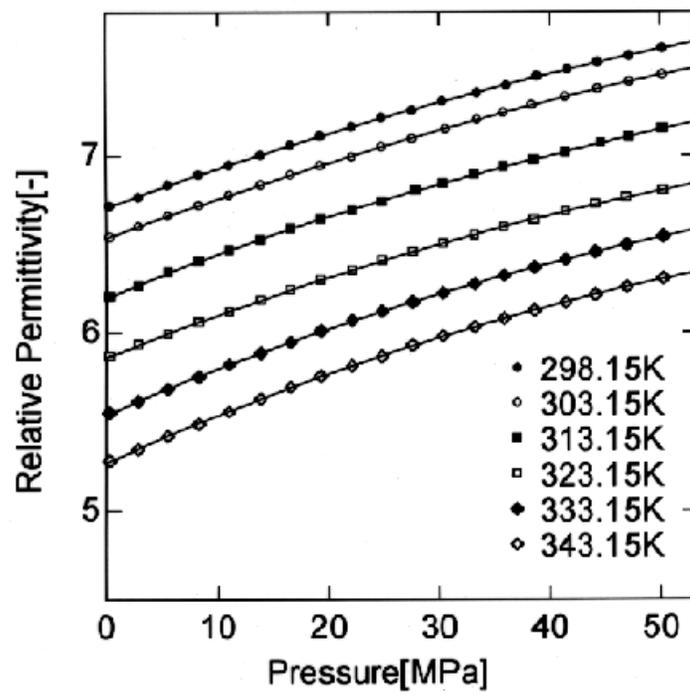


Fig.2

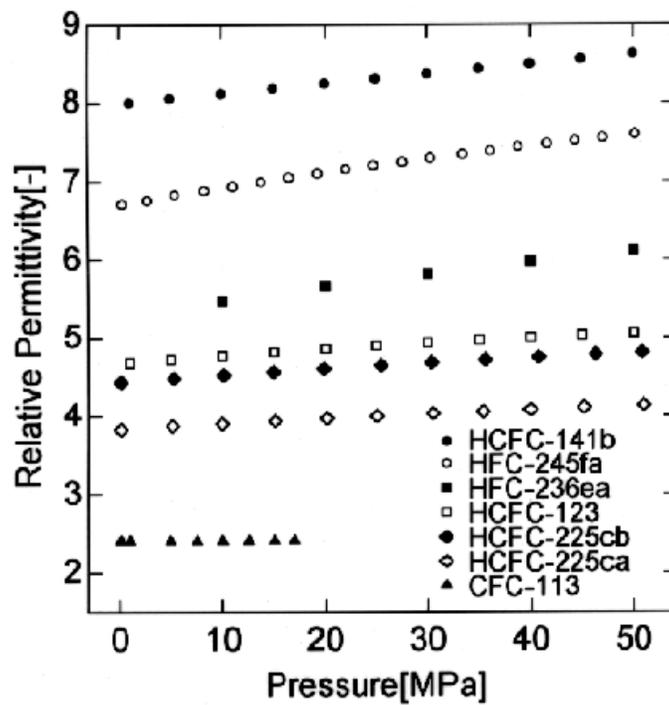


Fig.3

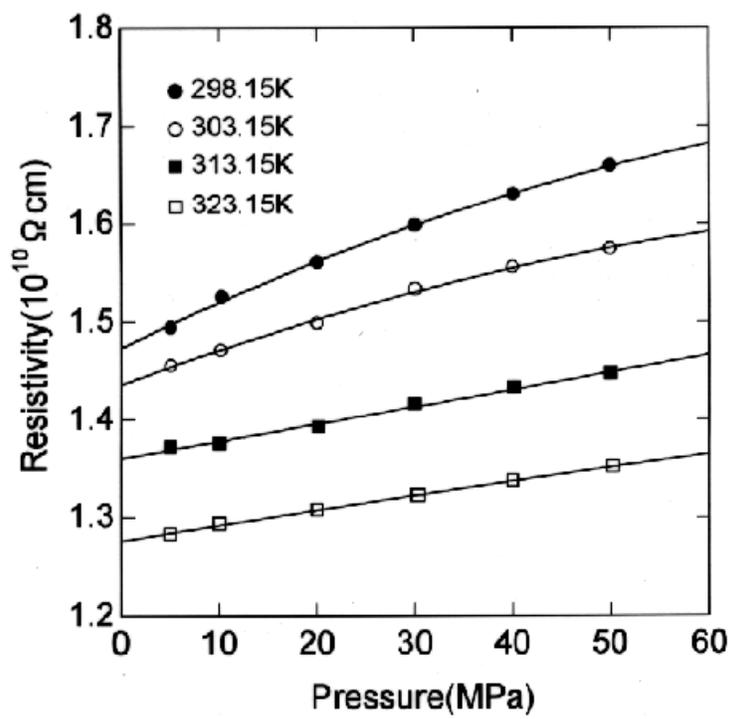


Fig.4